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METAL SURFACE DETERGENT
[Kinzoku hyomen senjozai]

Masayasu Hasegawa, et al.

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INVENTOR	(72): HASEGAWA, MASAYASU; YAMAGAMI, TOMOHIDE; SAKAI, NORIHITO; HAMADA, NOBUTAKE.
APPLICANT	(71): Nippon Synthetic Chem. Ind. CO. Ltd.
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[Claims]

[Clsim 1] Metal surface detergent consisting of polysaccharides having β-1,3-glucan produced by microorganisms belonging to genus Auerovacidium as its main chain and acid and/or chelate agent.

[Clsim 2] In Claim 1, the glucoses of the main chain of said polysaccharides contain β-1,3-glucan bond branches.

[Clsim 3] In Claim 1, said polysaccharides consist of β-1,3-glucan having three glucose branches with β-1,6 bonds per four glucoses of the main chain.

[Clsim 4] In Claim 1, said polysaccharides consist of β-1,3-glucan that has three β-1,6 bonds per four glucoses of the main chain and a group containing sulfur.

[Detailed Explanation of this Invention]

[0001] [Industrial Field]

This invention pertains to a metal surface detergent having an excellent effect of degreasing and rust inhibiting of metal surfaces.

[0002] [Conventional Technology]

The metal surface is coated with an oxide film during manufacturing and succeeding procedures and also polluted with grease, rust, and dust adhered while being mechanically processed or transported. Unless this soiled surface is cleaned before succeeding plating, chemical processing, and coating processes, such surface treatment cannot obtain strong adhesiveness to the metal surface, thus leading to unsatisfactory durability of the surface. Various

cleaning methods are conventionally used to clean the soiled metal surface, where an acid washing is most commonly used for chemically removing the rust. To wash the surface with an acid, first a metal is soaked in a detergent liquid containing appropriate ratios of acid (e.g., sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, fluoric acid, etc.) and additives (e.g., surface activation agent, lubricant, inhibitor, and solvent) to remove the rust and soil from the surface; then, the metal surface is immediately neutralized, rinsed, and dried.

[0003] [Method to Solve the Problems]

With the conventional acid washing method, as the process of removing rust and soil also causes erosion of the base of the metal, the metal must be immediately neutralized and water-washed after acid washing. Also, since the metal washed with acid is extremely susceptible to rusting, the next procedure must be performed immediately after acid washing, or, grease or rust inhibition oil must be applied to the metal surface prior to acid washing. However, when grease or oil is applied on the surface, a degreasing process for removing such material is necessary before performing the main manufacturing process, thus resulting in low productivity and cost inefficiency. Therefore, the industry needs a new metal cleaning method that can improve the entire process.

[0004] [Method to Solve the Problems]

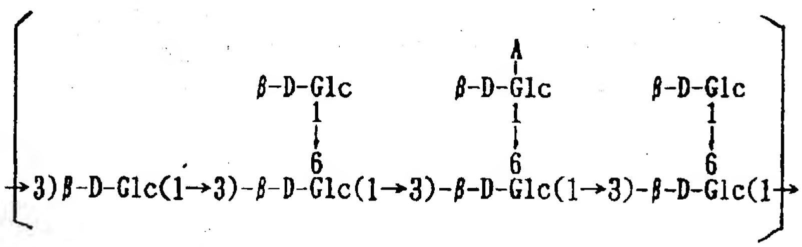
The developers of this invention investigated a new method to solve the problems described above and discovered that a metal surface detergent consisting of polysaccharides having β-1,3-glucan produced by microorganisms belonging to genus Auerovacidium as its main chain and acid and/or chelate agent could solve the problems experienced with the conventional method.

[0005] The metal surface detergent based on this invention comprises polysaccharides consisting of β-1,3-glucan produced by microorganisms belonging to genus Auerovacidium as its main chain and acid and/or chelate agent. An example of microorganisms belonging to genus Auerovacidium is Auerovacidium sp. K-1 No. 12989 (FERM P-12989) donated by the Microorganisms Industrial Technology Research Center of the Industrial Technological Institute.

[0006] The polysaccharides are not limited to specific materials as long as the main chain is β-1,3-glucan produced by microorganisms belonging to genus Auerovacidium. However, in most cases, the branched β-1,3-glucan has structural units expressed as Chemical expression 1 and Chemical expression 2 shown below (the total amount of both units per molecule is 1000 - 2000), and includes β-1,6 glucose branches containing a sulfur group. That is, in β-1,3-glucan cases, three out of four glucoses in the main chain have a respective glucose branch with a β-1,6 bond, and it includes sulfur at a ratio of 0.01 - 1.0 wt% per total weight of polysaccharides. Examples of

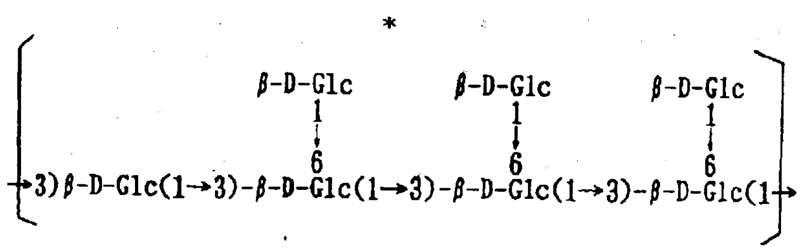
the group containing sulfur in this invention are sulfoacetic acid group, sulfonic acid group, polysulfonic acid group, cystein, cystine, methionine, etc. The methods to analyze the chemical and physical characteristics and structure of said polysaccharides can be found in "Science and Industry 64" (3), 131 - 135 (1990), and Agric, Biol, Chem, 47 (6) 1167 - 1172 (1983).

[0007] [Chemical Expression 1]



[where Glc designates glucose; A designates a group containing sulfur, such as sulfoacetic acid group, sulfonic acid group, polysulfonic acid group, cystein, and methionine.]

[0008] [Chemical Expression 2]



[0009] To obtain polysaccharides having β-1,3-glucan as its main chain, the method described below may be applied:

First, the following materials are added to microorganisms belonging to Auerovacidium:

Inorganic compound used as a carbon source (e.g., sucrose, glucose, or fructose); a nitrogen source (e.g., sodium nitric acid, ammonium nitric acid, or ammonium sulfuric acid); and other micro-factors necessary for growth, such as organic natural nitrogen source (e.g., enzyme extract, peptone, etc.), inorganic sulfur source (e.g., sulfuric acid magnesium, and sulfuric acid iron), metallic ion (e.g., magnesium, iron, etc.), and vitamins (e.g., ascorbic acid, pantothenic acid, etc).

The prepared mixture is cultured for 1 - 10 days, preferably for 2 days - 6 days, at 10°C - 60°C, preferably at 25°C - 35°C, with airflows. As a result, a culture liquid of polysaccharides having β-1,3-glucan as its main chain was acquired.

Another method is to obtain the same polysaccharides that, after collecting and washing the bacteria obtained by the method described above so as to prepare washed bacteria, the bacteria are contacted to a carbon source to obtain.

[0010] As a metallic detergent in this invention, the cultured liquid itself may be used as polysaccharides having β-1,3-glucan as its main chain, or a separation process may be provided to the liquid to separate the polysaccharides. To separate polysaccharides from the cultured liquid, bacteria are removed by a centrifugal-precipitation method or filtering method using a carrier, such as

sellite. Then, an applicable quantity of solvent (e.g., methanol, ethanol, isopropanol, etc.) or metallic ions (e.g., copper, aluminum) are added to cause precipitation. The deposited substance is dried using a dryer device such as drum dryer, and pulverized using a mill (e.g., hammer mill, ball mill, etc.) to prepare a powder material. To use this powder as a metal surface detergent, the powdered polysaccharides must be formulated to a water solution containing 5 wt% or less, preferably 0.1 - 1.0 wt% of polysaccharides. An amount exceeding 5 wt% causes excessive viscosity to eliminate the fluidity.

[0011] Examples of acid in this invention are inorganic acids (e.g., hydrochloric acid, sulfuric acid, phosphoric acid, and fluoric acid) and organic acids (e.g., oxalic acid, sulfamic acid and gluconic acid). Although it depends on the acid type and severity of rust and soil on the surface, the acid is usually acquired as a solution of 25% or less, preferably 5 - 15%. The composition quantity should be 5 - 30 (wt.) portions, preferably 10 - 20 (wt.) portions in terms of pure content thereto per 1 (wt.) portion of polysaccharides having β-1,3-glucan as its main chain.

[0012] The chelate agent in this invention is not particularly limited. Examples are (a) polyamino carboxylic acid group consisting of 1,2-cyclohexane diamine tetra acetic acid, diethylene triamine penta acetic acid, ethylene diamine di acetic acid, and ethylene diamine tetra acetic acid; (b) polyamino carboxylic acid group consisting of pyrophosphoric acid tri phosphoric acid, tri

methaphosphoric acid, and tetra methaphosphoric acid; and (c) oxycarboxylic acid group such as succinic acid. The chelate agent is usually adjusted to a solution of 10 wt% or less, preferably 0.1 - 5 wt%, at 1 - 20 (wt.) portions, preferably 0.2 - 10 (wt.) portions in terms of pure content thereto per 1 (wt.) portion of polysaccharides having β-1,3-glucan as its main chain. As described above, sufficient effect is produced when an acid or chelate agent alone is added to polysaccharides having β-1,3-glucan as its main chain. However, when combining the acid and chelate, the acid to chelate ratio (weight ratio) should be 0.5 : 1 - 10 : 1, preferably 1 : 1 - 5 : 1.

[0013] To wash a metal using the metal surface detergent based on this invention, any applicable technique can be used. Examples are: A metal is soaked in the detergent for 1 - 20 minutes; a metal is brushed while being soaked in the detergent; or a metal surface is sprayed and washed. The liquid temperature depends on the type of metal and degree of rust and soil on the surface. However, it is normally room temperature - 100°C, preferably room temperature - 40°C. When the cleaned metal needs to be sent to next procedure, the metal is washed with water and dried; if there is no succeeding procedure, the metal may be left untouched without providing any other process. That is, since the detergent based on this invention does not erode the base metal, immediate neutralization and water washing are not needed. Also, the cleaned metal can be left

untouched. Also, since the detergent based on this invention can form a rust-inhibiting film over the metal surface, rust can be prevented without applying grease or rust-inhibition oil. When the treated metal needs to be sent to next process, the rust-inhibiting film can be extremely easily removed by washing. The metal surface detergent based on this invention is effective to any type of metal surface (e.g., iron, copper, aluminum, brass, zinc, and stainless).

[0014] [Operation]

Since the metal surface detergent based on this invention can prevent erosion of metallic base and rust on the surface without applying grease or oil to the metal, the cleaning process can be simplified with a reduced number of operational steps. Therefore, the metal surface detergent that can improve the productivity and cost effectiveness is significantly advantageous to the industry.

[0015] [Operation]

The following explains the operational examples of this invention.

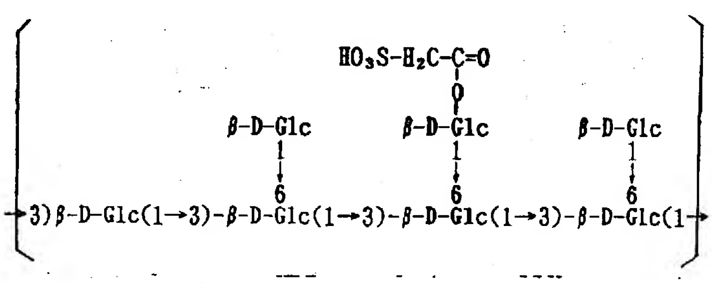
(Production of polysaccharides)

Microorganisms (FERM P-12989) belonging to Auerovacidium were cultured in a Zabeck culture (sucrose= 3%, sodium sulfuric acid=0.2%, potassium phosphoric acid= 0.1%, potassium chloride=0.05%, magnesium sulfuric acid-7 hydrate=0.05%, and sulfuric acid iron-7 hydrate=0.001%) at 27°C for 48 hours using an oscillation method. The obtained bacteria were used as seed bacteria and cultured at 27°C

for 96 hours using a 701 jar fermenter (airflow quantity = 501/min; stirring count = 300 rpm). The cultured liquid was filtered to remove bacterial. Then, isopropyl alcohol (1.2 times volume) was gradually added to acquired filtered liquid while the liquid was vigorously stirred. After the deposited polysaccharides were collected, the polysaccharides were soaked in an acetone tank, washed, dehydrated, and collected. The obtained fibers were dried at 70°C and pulverized using a feather mill.

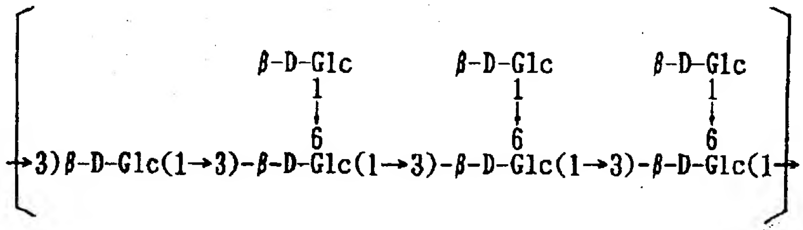
[0016] When acquired polysaccharides were analyzed [Science and Industry, 64 (3), 131-135 (1990) and Aglic, Biol. Chem., 47 (6) 1167-1172 (1983)], the structural unit could be expressed as Chemical expressions 3 and 4. The sulfur content was 0.05 wt% of the total polysaccharides. The combined structural unit count per molecule was approx. 1500.

[0017] [Chemical expression 3]



[where Glc designates glucose.]

[0018] [Chemical expression 4]



[where Glc designates glucose.]

[0019] <Detergent A>

200 ml of 16% hydrochloric acid were added to 200 ml solution containing 1.0 wt% of polysaccharides described above.

<Detergent B>

200 ml of 16% sulfuric acid were added to 200 ml solution containing 1.0 wt% of polysaccharides described above.

<Detergent C>

150 ml of 15% sulfuric acid and 50 ml of 10% succinic acid were added to 200 ml solution containing 1.0 wt% of polysaccharides described above.

<Detergent D>

150 ml of 21% sulfuric acid and 50 ml of 1.6 wt% ethylene diamine tetra acetic acid natrium solution were added to 200 ml solution containing 1.0 wt% of polysaccharides described above.

[0020] <Detergent E>

150 ml of 21% sulfuric acid and 50 ml of 10% succinic acid were added to 200 ml solution containing 1.0 wt% of polysaccharides described above.

<Detergent F>

Solution containing 0.5 wt% of polysaccharides described above.

<Detergent G>

8% hydrochloric acid

<Detergent H>

8% hydrochloric acid

<Detergent I>

0.2 wt% ethylene diamine tetra acetic acid natrium water solution

<Detergent J>

1.25% SUCCINIC ACID

[0021] <Detergent k>

200 ml of 16% hydrochloric acid were added to 200 mol of 1.0 wt% xanthane gum (KELZAN, product of Sansho) water solution.

<Detergent L>

200 ml of 0.4 wt% ethylene diamine tetra acetic acid natrium were added to 200 mol of 1.0 wt% xanthane gum (KELZAN, product of Sansho) water solution.

<Detergent k>

150 ml of 21% hydrochloric acid and 1.6 wt% of ethylene diamine tetra acetic acid natrium were added to 200 mol of 1.0 wt% xanthane gum (KELZAN, product of Sansho) water solution.

[0022] Operational example 1:

An iron test piece (6x8 cm) was soaked/washed in 150 g/l of hydrochloric acid (room temperature) according to JIS-Z0305, washed with water, and left untouched overnight to allow the entire surface to be rusted. This test piece was soaked in Detergent A (25°C). Then, the rust removal effect was observed immediately after the piece was taken out from Detergent A (I). Next, erosion condition of base metal was observed after 10 minutes of soaking (II). This iron test piece was taken out from a cleaning liquid and blow-dried. Then, 10 hours later, the rust on the test piece surface was observed (III). The results are shown in Table 1. The evaluation was rated according to the following system:

[0023]

(I) Rust removal effectiveness immediately after immersion

No rust was observed	-
One fourth of rust remained	+
Two forth of rust remained	++
Three fourth of rust remained	+++
Rust remained on the entire surface	++++

(II) Erosion of metallic base after 10 minutes of immersion

Entire body was eroded	X
Approx. 1/3 was eroded	Δ
No change on the surface	o

(III) Rust formation

Rust was formed on the entire surface	++++
Rust was formed on the 3/4 of the surface	+++
Rust was formed on the 2/4 of the surface	+++
Rust was formed on the 1/4 of the surface	+++
No rust was formed	-

[0024] Operational examples 2 - 5, Comparison examples 1 - 8:

The same method described in Operational example 1 was performed, except that Detergent A was replaced with the detergents shown in Table 1. The results are shown in Table 1.

[0025] [Table 1]

Detergent

Operational example

Comparison example

	使用した洗浄剤	(I)	(II)	(III)
実施例1	A	−	○	−
〃 2	B	−	○	−
〃 3	C	++	○	−
〃 4	D	−	○	−
〃 5	E	−	○	−
比較例1	F	++++	○	−
〃 2	G	−	×	++++
〃 3	H	−	×	++++
〃 4	I	+++	△	+++
〃 5	J	++	△	+++
〃 6	K	−	△	++
〃 7	L	++	△	++
〃 8	M	−	△	++

[0026] Operational examples 6 - 16, Comparison examples 9 - 16:

The same method described in Operational example 1 was performed, except that iron test piece was replaced with a copper test piece and the detergent shown in Table 2 were used. The results are shown in Table 2.

[0027] [Table 2]

Detergent

Operational example

Comparison example

	使用した洗浄剤	(I)	(II)	(III)
実施例6	A	−	○	−
〃 7	B	−	○	−
〃 8	C	+	○	−
〃 9	D	−	○	−
〃 10	E	−	○	−
比較例9	F	++++	○	−
〃 10	G	−	×	++++
〃 11	H	−	×	++++
〃 12	I	+++	△	+++
〃 13	J	++	△	+++
〃 14	K	−	×	++
〃 15	L	++	△	++
〃 16	M	−	×	++

[0028] [Effectiveness of this invention]

The metal surface detergent based on this invention can provide an excellent effect of rust inhibiting of metal surfaces without eroding the base of the metals.